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Proton-transfer compounds of 8-hydroxy-7-iodoquinoline-5-sulfonic acid (ferron) with 4-chloroaniline and 4-bromoaniline

Graham Smith,[a]* Urs D. Wermuth[a] and Peter C. Healy[b]

[a]School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane 4001, Australia, and [b]School of Biomolecular and Physical Sciences, Griffith University, Nathan 4111, Australia
Correspondence e-mail: g.smith@qut.edu.au

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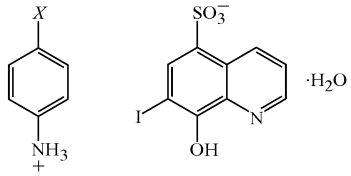
The crystal structures of the proton-transfer compounds of ferron (8-hydroxy-7-iodoquinoline-5-sulfonic acid) with 4-chloroaniline and 4-bromoaniline, namely 4-chloroanilinium 8-hydroxy-7-iodoquinoline-5-sulfonate monohydrate, $C_6H_7ClN^+\cdot C_9H_5INO_4S^-\cdot H_2O$, and 4-bromoanilinium 8-hydroxy-7-iodoquinoline-5-sulfonate monohydrate, $C_6H_7BrN^+\cdot C_9H_5INO_4S^-\cdot H_2O$, have been determined. The compounds are isomorphous and comprise sheets of hydrogen-bonded cations, anions and water molecules which are extended into a three-dimensional framework structure through centrosymmetric $R_2^2(10)$ O—H···N hydrogen-bonded ferron dimer interactions.

Comment

Ferron (8-hydroxy-7-iodoquinoline-5-sulfonic acid) is a bidentate complexing agent which has analytical applications as a selective colour reagent for the detection of iron(III) but not iron(II) (Vogel, 1964). The crystal structure of ferron (Merritt & Duffin, 1970; Balasubramanian & Muthiah, 1996) has shown the molecule to exist as a sulfonate–quinolinium zwitterion. This is also the case in the structure of the 1:1:1 adduct hydrate of ferron with urea (Smith *et al.*, 2004*b*). As a sulfonic acid, ferron is potentially capable of protonating most Lewis bases, but the crystal structures of only a small number of such salts have been reported to date. With 8-hydroxyquinoline a 1:1 sesquihydrate is formed (Smith *et al.*, 2004*a*), while with bifunctional 4,4′-bipyridine a monoprotonated 1:1 dihydrate is found (Hemamalini *et al.*, 2004). However, with guanidine carbonate, a dianionic ferron species is found in the hydrated compound $[(gu^+)_2(ferron)^{2-}]\cdot H_2O$ (Smith *et al.*, 2003). Since no compounds of ferron with aniline-type Lewis bases have been reported so far, and considering that anilines are particularly effective in giving stable crystalline salts with aromatic sulfonic acids, *e.g.* the 1:1 compounds of 5-sulfosalicylic acid with aniline (Bakasova *et al.*, 1991) and the 4-*X*-substituted anilines (*X* = F, Cl or Br) (Smith *et al.*, 2005), we attempted the preparation of compounds of the same Lewis base set with ferron in 50% ethanol–water solvent. The chemically stable 1:1 monohydrated crystalline title compounds 4-chloroanilinium 8-hydroxy-7-iodoquinoline-5-sulfonate monohydrate, (I), and 4-bromoanilinium 8-hydroxy-7-iodoquinoline-5-sulfonate, (II), were obtained using 4-chloroaniline and 4-bromoaniline, and their crystal structures are reported here. The reaction with 4-fluoroaniline resulted in the previously observed deiodination reaction of ferron, giving 8-hydroxyquinoline-5-sulfonic acid.



(I) *X*=Cl
(II) *X*=Br

The crystal structure determinations of (I) and (II) show the presence of three-dimensional hydrogen-bonded framework structures and confirm that these two compounds are isomorphous, which is consistent with previous observations (Dey & Desiraju, 2004) that, within the structures of both the 4-*X*-substituted anilines and 4-(4-*X*-phenoxy)-substituted anilines (*X* = Cl, Br, I and ethynyl), with only one exception (4-iodoaniline), all series members are isomorphous. Although the 4-chloro- and 4-bromoanilinium compounds with 5-sulfosalicylic acid are not isomorphous, they are found to be similar structurally (Smith *et al.*, 2005).

In (I) and (II), the anilinium group of the cation and the sulfonate O-atom acceptors of the anion interact head-to-tail and, together with the water molecule, give a cyclic hydrogen-bonded $R_3^3(8)$ (Bernstein *et al.*, 1995) association (the asymmetric unit) (Figs. 1 and 2). Further aminium···sulfonate and water···sulfonate interactions (Tables 1 and 2) form sheets which extend across the *bc* planes in the cell. These sheets are linked across the *a*-cell direction through centrosymmetric $R_2^2(10)$ cyclic hydrogen-bonded ferron···ferron dimer interactions between the 8-hydroxy donor and hetero-N-atom acceptor groups (Figs. 3 and 4). This represents the first

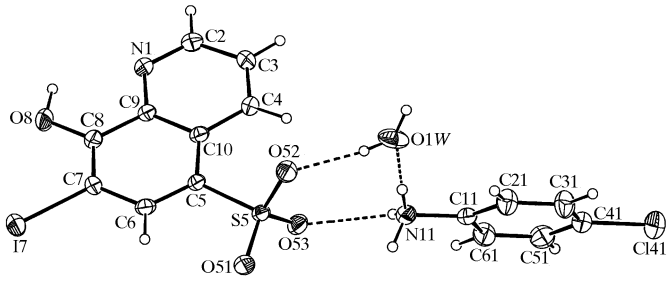


Figure 1
The molecular conformation and atom-numbering scheme for the individual cation, anion and water species in (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Inter-species hydrogen bonding is shown as dashed lines.

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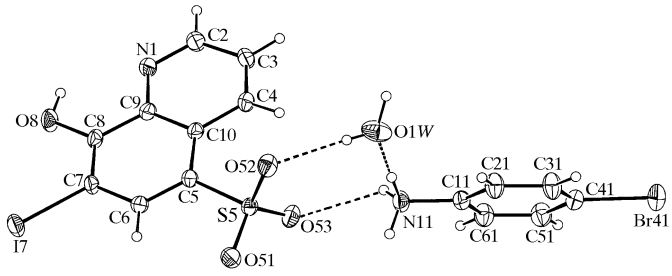

Figure 2
The molecular conformation and atom-numbering scheme for the individual cation, anion and water species in the isomorphous compound (II). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Inter-species hydrogen bonding is shown as dashed lines.

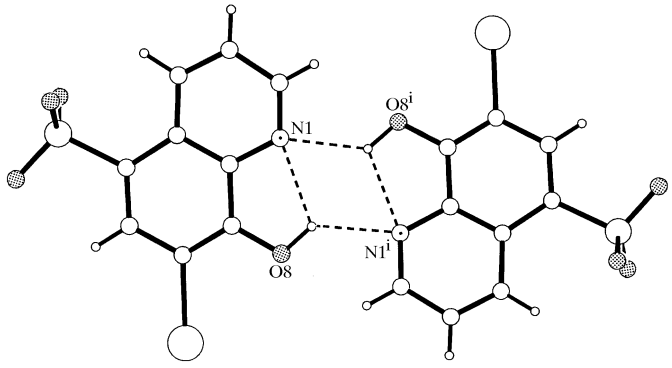

Figure 3
The centrosymmetric hydrogen-bonded (dashed lines) $R_2^2(10)$ ferron dimer found in (I) and (II). [Symmetry code: (i) $-x$, $-y+1$, $-z+1$.]

observed occurrence of this type of association in ferron structures, although a similar type of interaction is known in some of the adduct structures of the parent 8-hydroxyquinoline (oxine) (Hughes & Truter, 1979). It is usually precluded in ferron and its neutral adducts because of the presence of the sulfonate–quinolinium group zwitterion. In (I) and (II), three-dimensional framework structures are formed. Also found in the peripheral structure extension in (I) are Cl···Cl contacts [Cl41···Cl41^{v} = 3.538 (5) Å; symmetry code: (v) $-x+1$, y, $-z+\frac{3}{2}$]. In the isomorphous structure of (II), similar short Br···Br contacts [Br41···Br41^{v} = 3.612 (3) Å] are also found. Interionic aromatic ferron C2—H···O8^{i} interactions are also present [2.977 (7) Å in (I) and 2.998 (6) Å in (II); symmetry code: (i) $-x$, $-y+1$, $-z+1$].

With the ferron anion, the intra-ionic O8—H8···N1 hydrogen bond which is present in other nonzwitterionic compounds of ferron (Hemamalini *et al.*, 2004; Smith *et al.*, 2004*b*) is also found in both (I) and (II) [2.714 (6) and 2.707 (5) Å in (I) and (II), respectively]. Also, the common aromatic ring C6—H6···O51(sulfonate) association [2.857 (6) Å in (I) and 2.859 (5) Å in (II)] maintains the S5—O51 bond close to the plane of the aromatic ring [torsion angle C6—C5—S5—O51 = 3.8 (4)° in (I) and 3.1 (3)° in (II)].

Experimental

The title compounds were synthesized by heating solutions containing 8-hydroxy-7-iodoquinoline-5-sulfonic acid (ferron) (1 mmol) and, respectively, 4-chloroaniline (1 mmol) or 4-bromoaniline (1 mmol) in 50% ethanol–water (50 ml) for 10 min under reflux. After concentration to *ca* 40 ml, partial room-temperature evaporation of the hot-filtered solutions gave pale-brown flat prisms of (I) (m.p. 460.6–462.3 K) and large brown flat plates of (II) (m.p. 512.4–513.3 K).

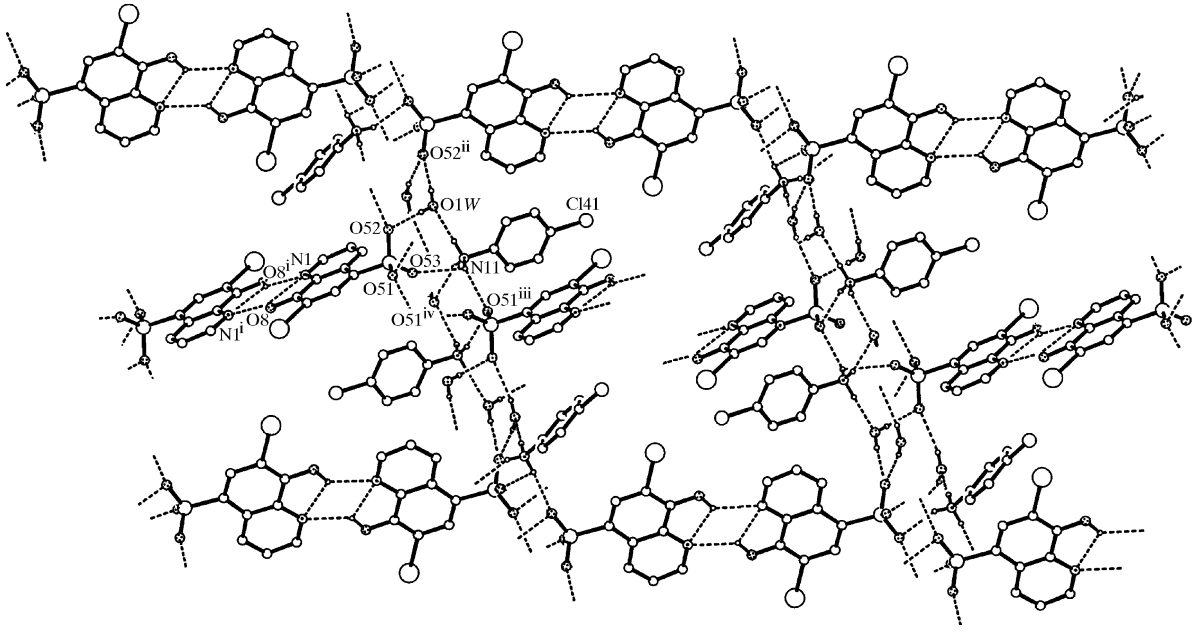

Figure 4
A perspective view of the packing of (I) in the unit cell, viewed down the approximate *b*-cell direction, showing hydrogen-bonding associations as dashed lines. This packing also represents that found in (II). See Table 1 for symmetry codes.

Compound (I)

Crystal data

$C_6H_7ClN^+\cdot C_9H_5INO_4S^-\cdot H_2O$
M_r = 496.70
Monoclinic, $C2/c$
a = 33.403 (10) Å
b = 5.902 (5) Å
c = 19.970 (7) Å
β = 114.56 (2)°
V = 3581 (4) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 2.08 mm^{-1}
T = 297 (2) K
0.40 × 0.25 × 0.20 mm

Data collection

Rigaku AFC-7*R* diffractometer
Absorption correction: ψ scan (*TEXSAN for Windows*; Molecular Structure Corporation, 1999)
T_{min} = 0.541, T_{max} = 0.660
4800 measured reflections
4108 independent reflections
3356 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
25 standard reflections
frequency: 150 min
intensity decay: 0.7%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.163
S = 1.10
4108 reflections
250 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.20 e Å^{-3}
$\Delta\rho_{min}$ = −1.09 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8···N1	1.00 (8)	2.19 (8)	2.714 (6)	111 (6)
O8—H8···N1^{i}	1.00 (8)	2.10 (8)	2.853 (6)	131 (7)
O1*W*—H1*W*···O52^{ii}	0.75 (6)	2.06 (6)	2.796 (5)	167 (6)
O1*W*—H2*W*···O52	0.85 (7)	1.99 (7)	2.822 (6)	168 (7)
N11—H11*A*···O53	0.87 (5)	2.42 (6)	2.781 (6)	106 (4)
N11—H11*A*···O51^{iii}	0.87 (5)	2.18 (5)	2.822 (6)	130 (5)
N11—H11*B*···O51^{iv}	0.85 (7)	2.10 (7)	2.902 (6)	157 (7)
N11—H11*C*···O1*W*	0.91 (6)	1.87 (6)	2.775 (7)	180 (9)
C2—H2···O8^{i}	0.95	2.43	2.977 (7)	116
C4—H4···O53	0.95	2.55	3.090 (6)	117
C6—H6···O51	0.95	2.43	2.857 (6)	107

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (iv) $x, y+1, z$.

Compound (II)

Crystal data

$C_6H_7BrN^+\cdot C_9H_5INO_4S^-\cdot H_2O$
M_r = 541.15
Monoclinic, $C2/c$
a = 33.494 (9) Å
b = 5.927 (4) Å
c = 19.963 (7) Å
β = 114.29 (2)°
V = 3612 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 4.13 mm^{-1}
T = 297 (2) K
0.25 × 0.20 × 0.20 mm

Data collection

Rigaku AFC-7*R* diffractometer
Absorption correction: ψ scan (*TEXSAN for Windows*; Molecular Structure Corporation, 1999)
T_{min} = 0.368, T_{max} = 0.436
4852 measured reflections
4153 independent reflections
3149 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
3 standard reflections
frequency: 150 min
intensity decay: 3.1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.110
S = 0.81
4153 reflections
250 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8···N1	0.84 (6)	2.19 (6)	2.707 (5)	120 (6)
O8—H8···N1^{i}	0.84 (6)	2.28 (7)	2.880 (5)	129 (6)
O1*W*—H1*W*···O52^{ii}	0.90 (6)	1.91 (6)	2.799 (5)	170 (6)
O1*W*—H2*W*···O52	0.80 (5)	2.04 (6)	2.833 (6)	170 (6)
N11—H11*A*···O53	0.86 (4)	2.47 (5)	2.778 (5)	102 (3)
N11—H11*A*···O51^{iii}	0.86 (4)	2.20 (4)	2.844 (5)	132 (4)
N11—H11*B*···O51^{iv}	0.81 (6)	2.12 (6)	2.889 (5)	160 (6)
N11—H11*C*···O1*W*	0.91 (5)	1.86 (5)	2.768 (6)	176 (5)
C2—H2···O8^{i}	0.95	2.44	2.998 (6)	117
C4—H4···O53	0.95	2.56	3.097 (5)	116
C6—H6···O51	0.95	2.44	2.859 (5)	107

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (iv) $x, y+1, z$.

H atoms involved in hydrogen-bonding interactions (H8, H11*A*, H11*B*, H11*C*, H1*W* and H2*W*) were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinements in calculated positions, with C—H = 0.95 Å, and were treated as riding atoms, with U_{iso}(H) = 1.2U_{eq}(C). In the case of (I), large residual difference electron-density peaks (maximum 1.20 e Å^{-3}) were located adjacent to the iodo substituent of the ferron anion.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3040). Services for accessing these data are described at the back of the journal.

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